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SPONSORED PROJECT TERMINATION

Date: JANUARY 21, 1977

Project Title: PROBLEMS IN HETEROCYCLIC CHEMISTRY

Project No: G-33-668

Project Director: DR. E. M. BURGESS

Sponsor: NATIONAL SCIENCE FOUNDATION

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G-33-668

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Syntheses and Reactions of Substituent Stabilized Thione Methylides

A. J. Arduengo, Edward M. Burgess

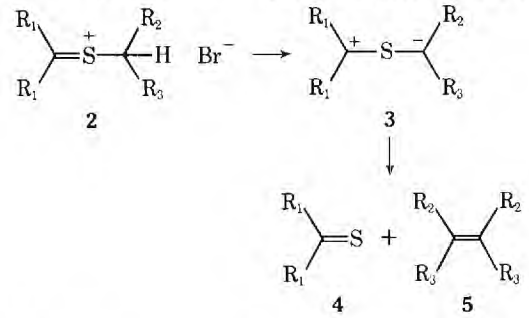
Syntheses and Reactions of Substituent Stabilized Thione Methylides

Sir:

Theoretical consideration of adjacent charge stabilization by sulfur d-orbital conjugation or polarization[1] and the mode of electronic transmission in π-systems containing sulfur has stimulated recent efforts to synthesize various thione ylides (**1**) in order to answer some of these questions.[2] From earlier work unperturbed noncyclic thione ylides appear to be unstable with respect to an electrocyclization to their thiirane valence tautomers[2a] whereas substitution by a combination of π-electron donating and accepting groups ("push–pull") provides sufficient charge stabilization to allow isolation of some representatives of this ylide system.[3] In this communication we wish to report on general synthetic routes to and chemical reactions of some stable thione methylides.

1

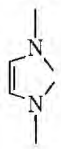
One synthetic approach was derived from consideration of the requirement for stabilizing substituents and led to selection of thiouronium salts as central intermediates whose base catalyzed deprotonation would provide **1**.[4] Tetramethylthiourea and *N,N'*-dimethylimidazolethione[5] were converted to the corresponding *S*-alkylthiouronium salts **2,** by reaction with the appropriate alkyl bromide in CH_2Cl_2 solution at 30°. Treatment of these salts with an equivalent of triethylamine in CH_2Cl_2 or THF solution at temperatures between −78 and 30° led to the immediate formation of the thione methylides, **3,** and triethylamine hydrobromide. Only ylides **3ya–c** and **3za–c** could be isolated at room temperature as crystalline solids which were characterized by their absorption in the ir ($CHCl_3$) at 1650–1700 cm^{-1} (C=O) or 2120–2140 cm^{-1} (C≡N) and consistent mass spectra.[6] Deprotonation of salts



2 **3** **4** **5**

y, R_1 = NMe_2

z, R_1 =

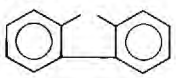


a, $R_2 = R_3 = CN$

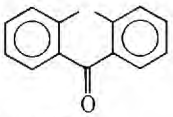
b, $R_2 = CN$; $R_3 = CO_2Et$

c, $R_2 = R_3 = CO_2Et$

d, $R_2 = R_3$ =



e, $R_2 = R_3$ =



f, R_2 = Ph; $R_3 = CO_2Et$

2y,z-d,f with triethylamine in THF at −78° produced solutions of transient ylides which upon warming to ca. −30° led to the formation of **4** and **5**.[7] The decomposition reaction observed for unstable thione methylides is analogous to those reported for many simple 1,2-sulfonium methylides.[8] No products derived from electrocyclic closure to a thiirane were apparent in such ylide decompositions.

As an alternative approach to the general construction of

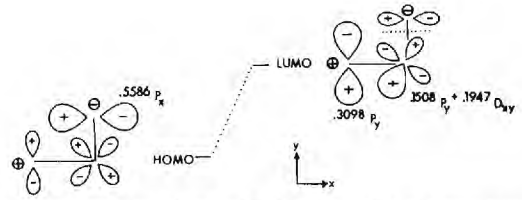
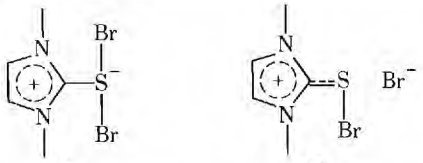


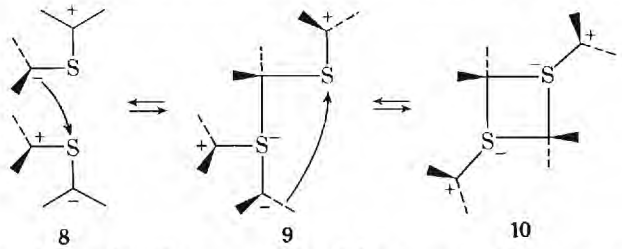
Figure 1. Representation of the HOMO and LUMO of **8** with calculated coefficients. The energy separation is ~11 eV.

such "push–pull" substituted ylides we have investigated the possibility of displacement at sulfur by carbon bases on the sulfurane **6**.[9] Our original expectations as to the potential site of substitution were realized when, for example, **6** underwent reaction with 2 equiv of sodio diethylmalonate in THF solution at 0° to provide **3zc.**[7] Such a sulfur ligand exchange reaction parallels those reported for other sulfuranes and probably involves the intermediacy of cation **7** which accepts a nucleophile at sulfur and not carbon.[10]

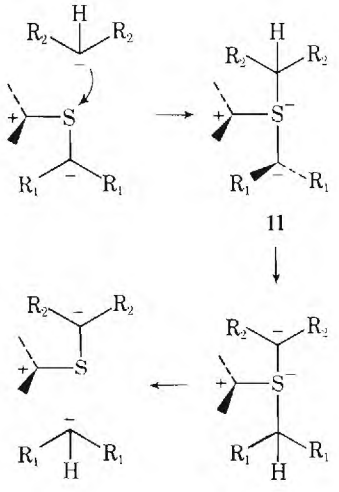


6 **7**

Upon admixture in CH_2Cl_2 solution at 30° a pair of thione methylides which are differentiated by nonidentical sets of π-donor and acceptor substituents undergo rapid ($t_{1/2}$ < 5 min) exchange of the latter substituent. For example, **3za** reacts with **3yc** to afford **3ya** and **3zc,** furthermore, the direction of this exchange reaction is enforced by the ready decomposition of **3ya** to **4y** and **5a.**[11] Similar ligand exchange reactions have been reported for sulfonium methylides and a degenerate ligand exchange mechanism has been suggested to account for the facile racemization of chiral sulfur in certain of these ylides.[12] The mechanism of substituent stabilized thione methylide multiple ligand exchange may be rationalized by a sequence (**8** → **10**) whose critical first step requires hypervalent bonding at sulfur rather than attack at the π-donor substituted carbon atom.[13] The intermediate **10** which resembles a bisulfurane stabilized by equatorial π-acceptor substituents but with considerable angle deviation in the apical CSC bonding system can fragment in two possible modes to effect the overall exchange observed. The proposed CS bonding established in **8** is supported by an inspection of the frontier HOMO and LUMO eigenvectors for a model ylide as determined by a SCF-CNDO2 calculation.[14] The HOMO is primarily the carbanion p_x orbital while the LUMO has a greater sulfur p_y contribution than the carbocation p_y (Figure 1)[15] which suggests initial CS union to form sulfurane **9** is the controlling frontier orbital interaction and the same argument also applies to **7.** In a related reaction **3ya** and sodio diethylmalonate in THF solution of 30° gives **3yc** and malononitrile.[7] Again, we visualize this ligand displacement process as proceeding through hypervalent intermediates **11** and **12.**[16] Finally, the thione methylides derived from *N,N'*-dimethylimidazolethione as a precursor undergo a facile reaction with tetramethylthiourea in CH_2Cl_2 solution at 0–30° to afford this



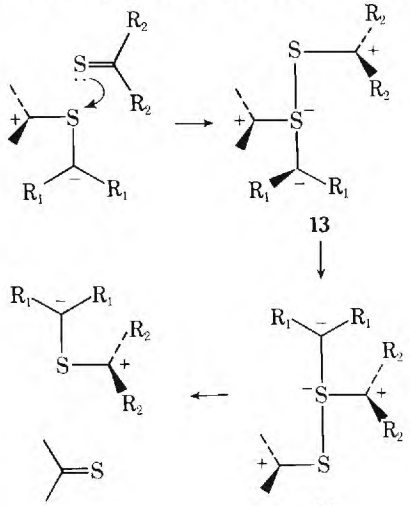
8 **9** **10**



11

12

bis(dimethylamino)-substituted ylides.[7] This process, which is equivalent to ligand transfer between ylide and thione, appears to proceed in a direction to provide the ylide with the less effective π-electron donor substituents. Rationalizing this behavior in a manner consistent with the other observed multiple ligand exchange and displacement reactions requires an intermediate **13** in which the equivalent of a 1,2-shift of the π-electron rich group occurs to give **14;** the driving force for



13

14

the shift is dictated by the formation of the most stable sulfurane as determined by the electron withdrawing ability of the equatorial substituent. In conclusion, the general features of the chemistry of highly perturbed thione methylides closely resemble those of sulfuranes and are certainly unlike those of the unperturbed congeners.

Acknowledgments. We sincerely wish to thank the National Institutes of Health, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for research grants.

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(1) For an excellent discussion, see C. A. Coulson, Proceedings of the Robert A. Welch Foundation Conferences on Chemical Research XVI. Theoretical Chemistry, 1973, pp 61–117.
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(3) Thione methylides have been isolated from the reaction of trithiones with electrophilic diazo compounds (S. Tamagaki and S. Oae, *Tetrahedron Lett.*, 1159 (1972)) and from thioureas and 2,2-dicyano-3,3-bis(trifluoromethyl)-oxirane (W. J. Middleton, *J. Org. Chem.*, **31,** 3731 (1966)).
(4) This approach was reported to be unsuccessful by earlier workers. M. Takaku, S. Mitamura, and H. Nozaki, *Tetrahedron Lett.*, 3651 (1969).
(5) R. Grigg, T. J. King, and G. Shelton, *Chem. Commun.*, 56 (1970).
(6) Satisfactory (±0.3%) elemental analysis (C, H, N, S) have been obtained for all new isolated compounds.
(7) Identified by mixture melting point and/or ir spectral comparison with authentic samples.
(8) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84,** 3782 (1962); **87,** 1353 (1965); A. W. Johnson, V. J. Hruby, and J. L. Williams, *ibid.*, **86,** 918 (1964); V. Franzen and H. E. Driessen, *Chem. Ber.*, **96,** 1881 (1963); C. G. Swain and E. R. Thornton, *J. Am. Chem. Soc.*, **83,** 4033 (1961).
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(10) J. C. Martin and L. J. Kaplan, *J. Am. Chem. Soc.*, **95,** 793 (1973); J. C. Martin and R. J. Arhart, *ibid.*, **93,** 2339 (1971).
(11) We exclude an ylide to carbene dissociative mechanism by our failure to obtain trapped carbene products with added thioethers or alkenes.
(12) H. Nozaki et al., *Tetrahedron*, **23,** 4279 (1967).
(13) This proposal has certain features in common with the proposed mechanisms for chiral sulfoxide and sulfimide interconversions. D. J. Cram, F. G. Yamagishi, D. R. Rayner, and E. T. Zwicker, *J. Am. Chem. Soc.*, **95,** 1916 (1973); D. J. Cram, D. C. Garwood, and M. R. Jones, *ibid.*, **95,** 1925 (1973).
(14) The geometrical parameters used were those of **2zc** as determined by x-ray crystallography. A. J. Arduengo and E. M. Burgess, *J. Am. Chem. Soc.*, following paper in this issue.
(15) The calculated composition of π-LUMO at sulfur is $0.1508p_y - 0.1947d_{xy} - 0.0567p_x$ and the resultant hybrid is shown in Figure 1.
(16) An analogous mechanism has been proposed for ligand displacements at selenium in ylides. S. Tamagaki and K. Sakaki, *Tetrahedron Lett.*, 1059 (1974).

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Received February 18, 1976

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Tricoordinate Hypervalent Sulfur Compounds

ABSTRACT

1,3-Dimethylimidizolthione (1) reacts with bromine to give 1,3-dimethylimidizolthione S,S-dibromide whose hypervalent structure was predicted by semiempirical molecular orbital calculations and verified by x-ray crystallography. The hypervalent S,S-dibromide and S,S-iodobromide were also prepared. Compound 1 reacts with cyanogen bromide to the salt, 2-thiocyanato-1,3-dimethylimidizolium bromide, according to an x-ray structure determination. An explanation is offered for these different results.

Tricoordinate Hypervalent Sulfur Compounds

Sir:

Molecular multicenter bonding which occurs when a given atom has more bonds than atomic orbitals as defined by the octet rule is termed hypervalent and many examples are found among the second and third row main-group elements. Aside from an enormous amount of theoretical interest[1] in such "orbitally deficient" molecules they also have found increasing importance as synthetic organic reagents and especially noteworthy this latter regard is the work of Martin et. al.[2] on tetracoordinate tetracovalent sulfuranes. We now wish to report on a new class of hypervalent sulfur molecules, which are tricoordinate and tricovalent and have unique stability as compared to their tetracovalent counterparts.

Figure 1. Axial bonding system in tetracovalent sulfuranes.

The trigonal bipyramidal geometry observed[3] for tetracovalent sulfuranes, is a result of the enforced 3-center linear axial (z) orbitally-deficient bonding arrangement whose orbitals are simplified in Fig. 1. In such molecules electrons are required to fill high-lying nonbonding orbitals (n_z) centered on the apical ligands (X). This leads to bonding only from the 2-electron 3-center orbital array σ_z while the balance of the axial electron density must be delocalized away from the central atom toward the ligands and

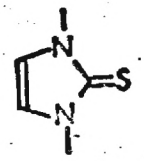
thus stabilization is achieved by increasing electronegative apical groups. The effect of higher order (for S, 3d or 4s) orbitals on the central atom in the basis set on the calculated Hartree-Fock energy seems to be minimal[1]. Use of these more diffuse orbitals which have the proper symmetry to mix with n_z (i. e., dz^2 in Fig. 1) seems to serve only the purpose of an improved basis set allowing a small shift in electron density from ligand to the central atom. Hypervalent sulfur molecules would experience a stabilizing total energy decrease if ligand electron density could be delocalized to a equatorial substituent and this could be accomplished by the placement of a low-lying π-acceptor substituent orbital of proper symmetry centered in the equatorial plane. The two possible orientations of this acceptor orbital with the axial XSX bonding system are parallel and orthogonal. The symmetry for interaction of a parallel π-acceptor (p) with the axial σ_z orbital and the ligand nonbonding orbital (n_z-n_z), is shown in Fig. 2. Rotation allows interaction of the π-acceptor with the axial ligand central atom non-bonding levels (n_x+n_x+n_x) and (n_x-n_x+n_x) with the resultant stabilization as shown in Fig. 3. We must conclude that the latter alignment is favored and calculate the total energy difference to

Figure 2. Axial interaction diagram for a parallel acceptor orbital.

be ~12 kcal/mole for a hypothetical geometry-optimized tricoordinate sulfurane, H_2CSCl_2.[4] The energetic placement of the low-lying -acceptor orbital is critical and the 6 π-electron aromatic imidazolium cation appeared to be a suitable synthetic candidate for this substituent.

Figure 3. Axial interaction diagram for an orthogonal acceptor orbital.

Reaction of 1,3-dimethylimidazolthione[5] (1) with one-half equivalent of bromine at 0° in CH_2Cl_2 solution gives the disulfide 2a,[6] mp 240-1°(dec). Further bromination of 2a under the same conditions affords in high yield the stable tricoordinate tricovalent sulfurane 3a, mp 173-4°(dec).



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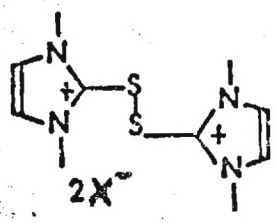

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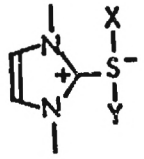

3

a, X= Y = Br

b, X = Y = Cl

c, X = Br, Y = I

A single crystal of 3a was analyzed by x-ray diffraction: monoclinic, a = 8.018, b = 14.396, c = 16.403, β= 95.53, V = 1893 $\mathring{A}^3$, Z = 8, ρ_{calcd} = 2.029 g/cm^3, space group $P2_1/C$ from systematic absences, hol, when l = 2n+1, oko, when k = 2n+1, Mo K αX-radiation at a takeoff angle of 6.5 using a SYNTEX P_{2_1} diffractometer. A total of 3254 nonzero reflections were refined to a crystallographic R factor of 0.062 and the resultant structure is shown in Fig. 4.

Figure 4. Solid state geometry of sulfurane 3a.

In complete agreement with the theoretically derived geometry this sulfurane has an axial 3-center geometry almost colinear (θ = 87. ± .8) with elongated bonds of 2.520 and 2.477 ± .077) Å (cf. 2.3 A in S_2Br_2). The equatorial C—S bond length is 1.730± .02 Å as compared with 1.695 Å in 1[7]. It should be noted that 3 participates via a nonplanar geometry (ζ = 90.0°) in the interaction qualitatively described in Fig. 2, presumably due to the steric effect of the C-5 and C-4 methyl groups. Had planarity been possible, an even more stable structure should have resulted. Analogous tricoordinate sulfuranes, 3b, mp 157-8° (dec) and 3c, mp 147-50 (dec); result from the reaction of 1 in CH_2Cl_2 solution at 0° whith chlorine and iodine monobromide, respectively. The latter sulfurane begins to decompose in the solid state after ca. 1 hour at room temperature which, nevertheless, represents extraordinary thermal stability considering the low dissociation energy of a normal two electron S—Br and S—I bond which here has an even lower bond order.

In constrast, the reaction of 1 with cyanogen bromide give the salt 4a, mp 220-1° (dec) whose crystal structure was determined similarily by x-ray diffraction: monoclinic, a = 7.288, b = 9.502, c = 15.206, β = 122.459, V = 1053 Å^3, Z = 4, ρ_{calcd} = 3.381 g/cm^3, space group $P2_1/C$ from systematic absences. A total of 1248 nonzero reflections were refined to a crystallographic R factor of 0.043 and the resultant structure is shown in Fig. 5.

Figure 5. Solid state structure of salt 4a.

The covalent attachment of the cyano group is characterized by an axial S—C bond length of 1.757 Å orthogonal (θ = 96.20°, ζ = 90.0) to the ring system while the equatorial bromide ion occupies a lattice position 3.270 Å distant from sulfur. A second neighbor bromide ion was found at a lattice position 3.587 Å in the axial direction from C2 anti to the cyano group.

Treatment of 1 with cyanogen chloride gives 4b, mp 215-6 (dec) and the common ionic structure of these derivatives was evident from their superimposible ir spectra.

4, a, X = Br

b, X = Cl

The observed incongruity between the appearace of a hypercovalent or an ionic molecule as a function of ligand structure is clearly independent of ligand electronegativity. If one considers an electron-rich linear multicenter bonding array with the hypervalent center participating by predominately p-orbital bonding two general patterns of occupied, symmetry-adapted, delocalized molecular orbitals appear. For 2n+3 (n = 0,1,2...) atomic orbitals combined to give molecular orbitals 2n+4 electrons there are 1n+1 occupied non-bonding levels with respect to the ligands which do not contribute to vicinal bonding in the array and for isolable hypervalent molecules requires electronegative ligands to stabilize the resultant electron density as is observed for 3. Conversely, 2n+4 atomic orbitals combined to give molecular orbitals for 4n+6 electrons result in 4n+2 occupied anti-bonding levels noded with respect to the ligands which are destabilizing regardless of ligand electronegativity, as for example, the hypervalent possibility related to 4. In other words, if the sum of the one central hypervalent atom plus the coaxial ligand atoms is odd the system is stable and, if even, destabilized. This argument may be extrapolated to account for the origin of the unusally high energy barrier observed for the gas-phase nucleophilic displacement at carbon associated the reaction of CN^- with CH_3Cl and C_2H^- with CH_3F which requires a linear transition state described by a combination of 2n+4 atomic orbitals.[7] Likewise the observed highly concerted decomposition ($\Delta H^{\ddagger}$ = 17.6 kcal/mole) of di-t-butyl O, O'-phenylbisthioperbenzoate proceeds via a linear 6-electron 5-center hypervalent sulfur bonding array with one occupied bonding and two occupied non-bonding levels in the transition state and is an example of a stabilized 2n+3 atomic orbital combination.[8]

Acknowledgements.

We sincerely wish to thank the N.I.H. and N.S.F. for research grants and to Professor Charles Liotta and J. C. Martin for bringing references (7) and (8) to our attention.

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(8) J. C. Martin and M. M. Chau, ibid., 96, 3319 (1974).

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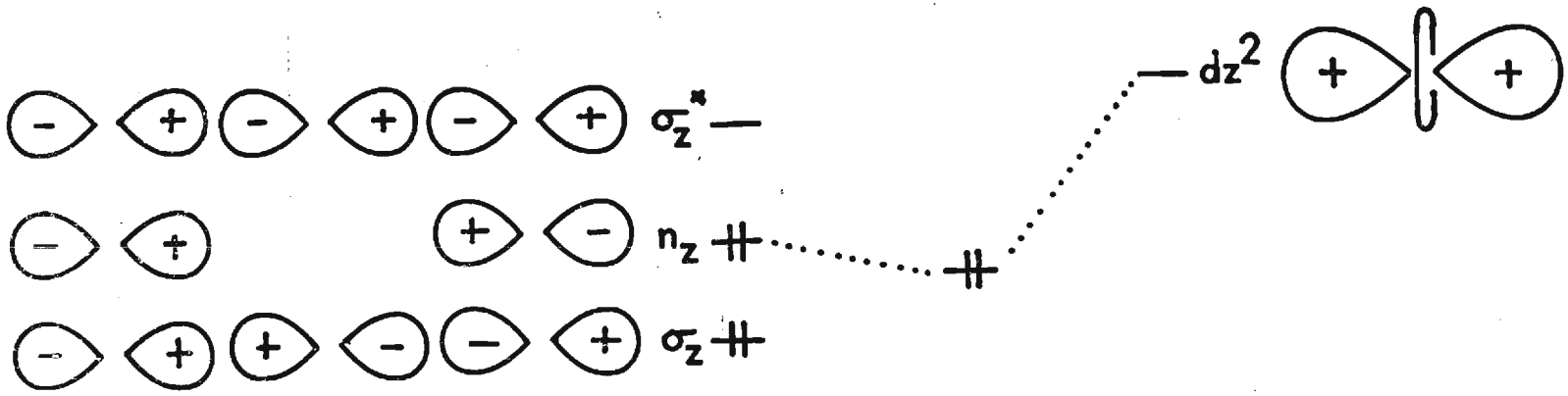
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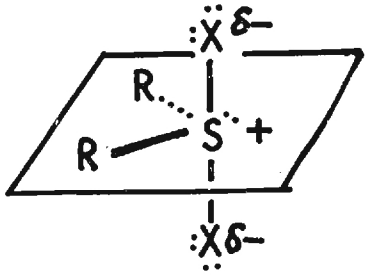
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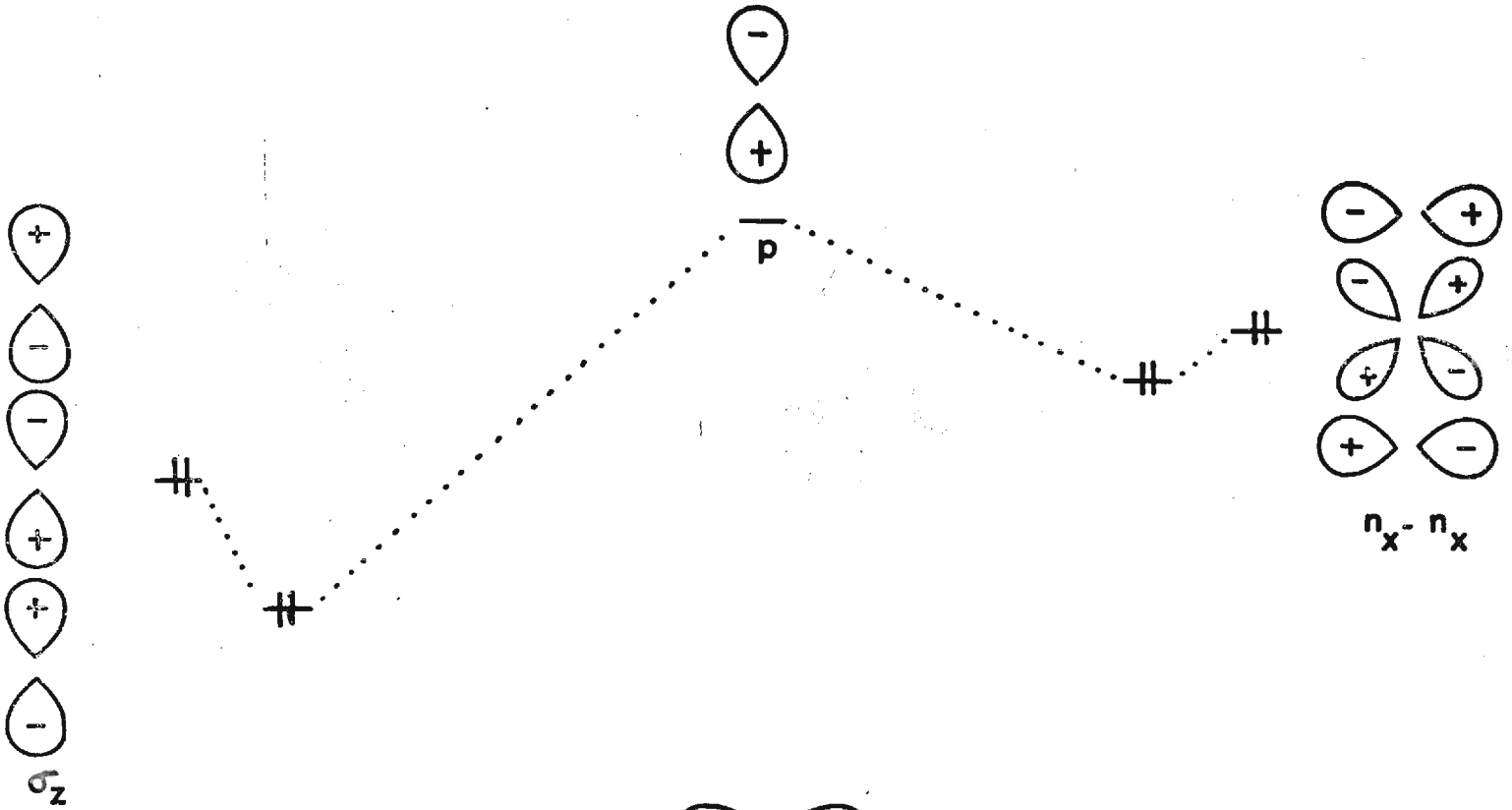
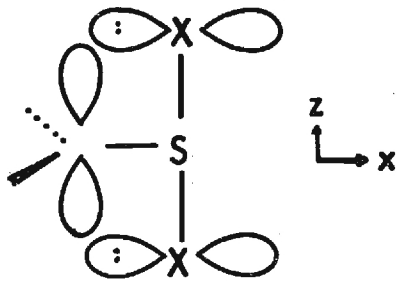
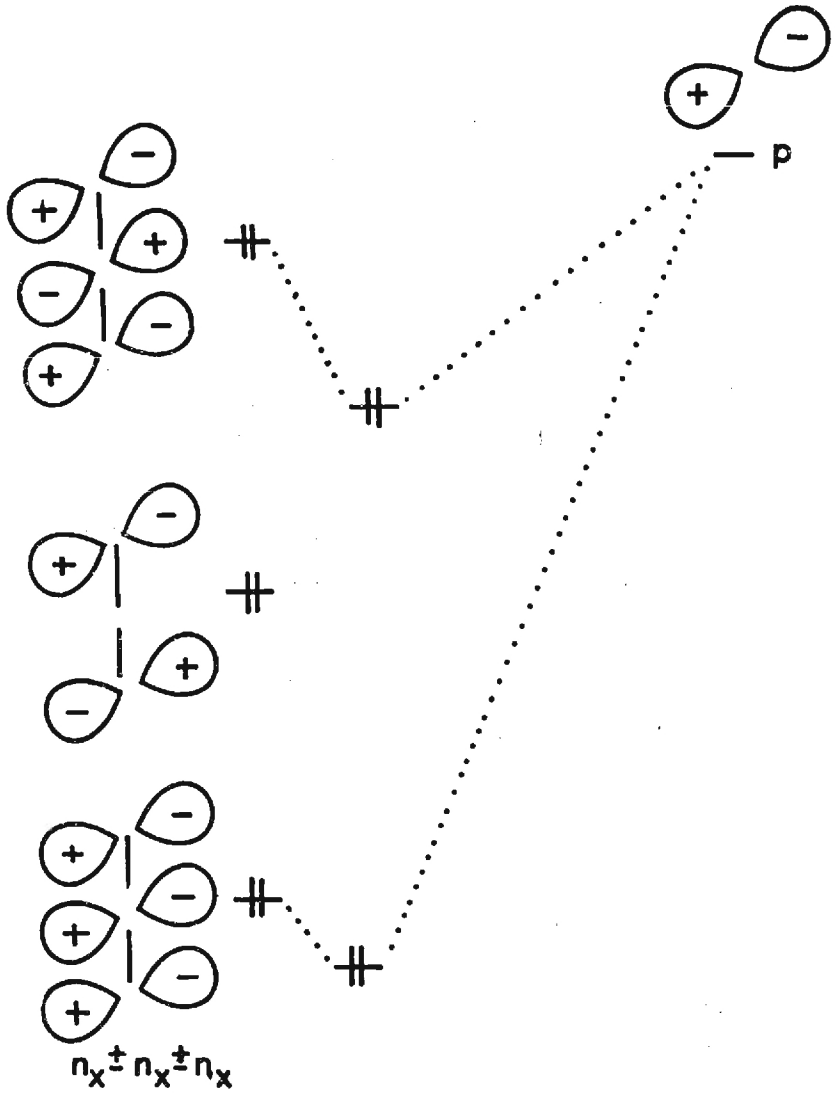
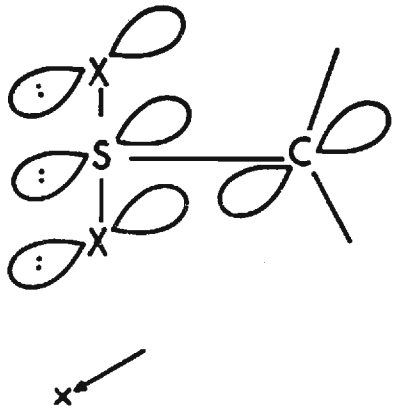
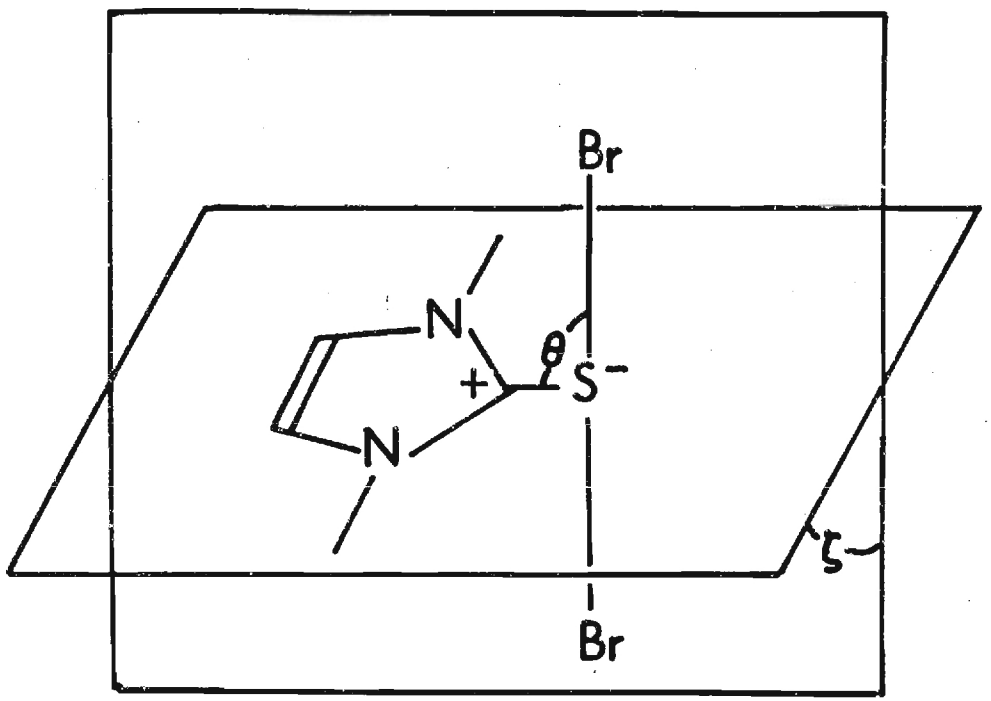
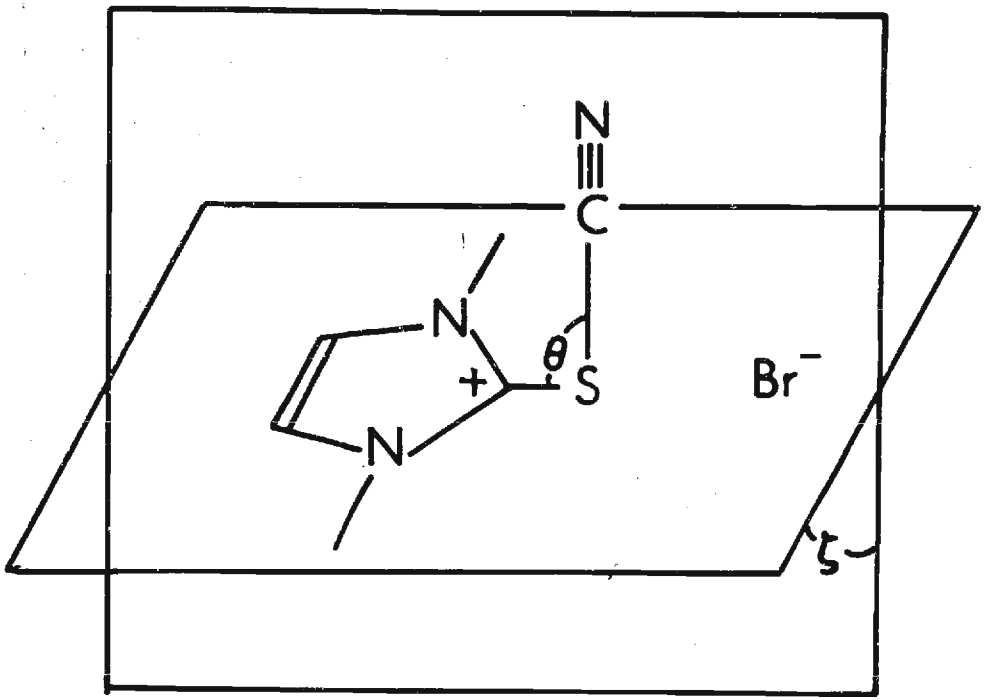

p
σ_z
$n_x - n_x$


X
S
X
z
x


p
$n_x \pm n_x \pm n_x$


X
S
C
X


Br
N
θ
+
S⁻
N
ζ
Br


N
C
N
θ
+
S
Br⁻
N
ζ

G-33-668

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

OFFICE OF
THE DIRECTOR OF
FINANCIAL AFFAIRS

February 16, 1977

Grants and Contracts Office
National Science Foundation
Washington, D. C. 20550

Gentlemen:

Enclosed is the original and two copies of the final fiscal report for grant number MPS75-08779 A02, formerly GP-38755X.

If you have any questions or desire additional information, please let me know.

Sincerely yours,

C. Evan Crosby

C. Evan Crosby
Associate Director of
Financial Affairs

CEC/bs
enclosure:

cc: Dr. E. M. Burgess
Mr. E. E. Renfro
Mr. A. H. Becker
File G-33-668

NATIONAL SCIENCE FOUNDATION
Washington, D.C. 20550

RESEARCH GRANT
BUDGET & FISCAL REPORT

Form Approved
Budget Bureau No. 99-R0013

Please read instructions on reverse side carefully before completing this form.

INSTITUTION AND ADDRESS	NSF PROGRAM	GRANT PERIOD / REPORTING PERIOD
Georgia Institute of Technology Atlanta, Georgia	Synthetic Organic	GRANT PERIOD from 7/1/73 to 12/31/76 REPORTING PERIOD from 7/1/73 to 1/31/77*

GRANT NUMBER	BUDGET DUR. (MOS.)	PRINCIPAL INVESTIGATOR(S)	GRANTEE ACCOUNT NUMBER
MPS73-08779 A02	XX 42	Burgess	G-33-668

	NSF Funded Man Months Cal.	Acad.	Summ.	NSF AWARD BUDGET	CUMULATIVE GRANT EXPENDITURES *Do Not Round*
A. SALARIES AND WAGES					
1. Senior Personnel					
a. 1 (Co)Principal Investigator(s)			2	$ 4,222	
b. Faculty Associates					
Sub-Total				$ 4,222	$ 1,677.00
2. Other Personnel (Non-Faculty)					
a. Research Associates—Postdoctoral					
b. Non-Faculty Professionals					
c. 2 Graduate Students				9,400	
d. Pre-Baccalaureate Students					
e. Secretarial—Clerical					
f. Technical, Shop, and Other					
TOTAL SALARIES AND WAGES				$ 13,622	$ 35,175.65
B. STAFF BENEFITS IF CHARGED AS DIRECT COST				370	142.55
C. TOTAL SALARIES, WAGES, AND STAFF BENEFITS (A + B)				$ 13,992	$ 35,318.20
D. PERMANENT EQUIPMENT					7,824.99
E. EXPENDABLE EQUIPMENT AND SUPPLIES				3,000	11,336.83
F. TRAVEL 1. DOMESTIC (INCLUDING CANADA)				300	906.00
2. FOREIGN					-0-
G. PUBLICATION COSTS				1,000	581.95
H. COMPUTER COSTS IF CHARGED AS DIRECT COST					-0-
I. OTHER DIRECT COSTS					
Professional Services					324.00
J. TOTAL DIRECT COSTS (C through I)				$ 18,292	$ 56,291.97
K. INDIRECT COSTS					
65% of salaries and wages				8,854	22,316.06**
L. TOTAL COSTS (J plus K)				$ 27,146	$ 78,608.03
Less Residual Funds				6,721	
M. AMOUNT OF THIS AWARD (ROUNDED)				$ 20,400	
N. CUMULATIVE GRANT AMOUNT				$ 79,600	
O. UNEXPENDED BALANCE (N. BUDGET MINUS L. EXPENDITURE)					$ 991.97

REMARKS: Use extra sheet if necessary

*No obligations were incurred outside the grant period of 7/1/73 thru 12/31/76.

**57% of $12,444.00= $ 7,093.98
65% of 7,848.00= 5,101.40
68% of 14,883.35= 10,120.68
$22,316.06

FOR NSF USE ONLY
Final Fiscal Report Accepted
Grant Closed _____ Remains Open _____
By _____ Date _____
Grants Administration Section, Area _____

SIGNATURE OF PRINCIPAL INVESTIGATOR	TYPED OR PRINTED NAME	DATE
E M Burgess	E. M. Burgess	2-4-77

I CERTIFY THAT ALL EXPENDITURES REPORTED ARE FOR APPROPRIATE PURPOSES AND IN ACCORDANCE WITH THE AGREEMENTS SET FORTH IN THE APPLICATION AND AWARD DOCUMENTS

SIGNATURE OF AUTHORIZED OFFICIAL	TYPED OR PRINTED NAME & TITLE	DATE
C. Evan Crosby	C. Evan Crosby, Associate Director of Financial Affairs	2-16-77

FOR NSF USE ONLY

Organ. Code	F.Y.	Fund ID	Prog. Code	Ob. Class	O/Dres.	Award No.	Amd.	Inst. Code	Unexpended Balance	Trans.	Lot
									$		

NSF Form 98, JULY 1971

SUPERSEDES ALL PREVIOUS EDITIONS

NATIONAL SCIENCE FOUNDATION
Washington, D.C. 20550

SUMMARY OF COMPLETED PROJECT

Form Approved
OMB No. 99R0013

Please read instructions on reverse carefully before completing this form.

1. INSTITUTION AND ADDRESS	2. NSF PROGRAM	3. GRANT PERIOD
Georgia Institute of Technology Atlanta, Georgia 30332	Problems in Heterocyclic Chemistry	from 7/1/73 to 12/31/76

4. GRANT NUMBER	5. BUDGET DUR. (MOS)	6. PRINCIPAL INVESTIGATOR(S)	7. GRANTEE ACCOUNT NUMBER
MPS73-08779(Formerly GP-38755X1)	42	Edward M. Burgess	G-33-668

8. SUMMARY (Attach list of publications to form)

SCF semiempirical calculations suggest that substituent perturbed thione methylides should have non-planar structures. An x-ray crystallographic analysis of N-,N-dimethylimidazolthione S-dicarboethoxymethylide supports this conclusion. NMR C^{13} and H^{1} shifts in this methylide vs. some model compounds may be correlated with the SCF bond orders and used to qualitatively describe the π-conjugation between the charged centers in these 1,3-dipoles.

The deprotionation of S-dialkylthiouronium salts with appropriate electron withdrawing β-substituents provides the thiourea S-disubstituted methylides. These 1,3-dipoles also result from the treatment of S-dibromothiourea (sulfuranes) with carbon bases and exhibit a number of interesting reactions such as ylide ligand-ligand exchange, decomposition to alkenes, and ligand trahsfer from ylide to thione.

1,3-Dimethylimidizolthione (1) reacts with bromine to give 1,3-dimethylimidizolthione S,S-dibromide whoe hypervalent structure was predicted by semiempirical molecular orbital calculations and verified by x-ray crystallography. The hypervalent S,S-dibromide and S,S-iodobromide were also prepared. Compound 1 reacts with cyanogen bromide to the salt, 2-thiocyanato-1,3-dimethylimidizolium bromide, according to an x-ray structure determination.

9. SIGNATURE OF PRINCIPAL INVESTIGATOR/ PROJECT DIRECTOR	TYPED OR PRINTED NAME	DATE
Edward M. Burgess	Edward M. Burgess	2/7/77

NSF Form 98A (5-76)

G-33-668

Final Report

NSF Grant MPS73-08779

July 1, 1973, to December 31, 1976

Publications

The following publications resulted from studies supported by the title grant:

Synthesis and Cycloadditon Reactions of Fluorenethione S-Benzoylimide.
E. M. Burgess and H. R. Penton, Jr., J. Org. Chem., 39, 2885 (1974).

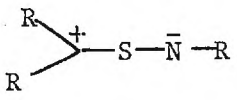
Synthesis and Reactions of Substituent Stabilized Thione Methylides.
E. M. Burgess and A. J. Arduengo, J. Amer. Chem. Soc., 98, 5020 (1976).

The Structure of a Substituent Stabilized Thione Methylide
E. M. Burgess and A. J. Arduengo, J. Amer. Chem. Soc., 98, 5021 (1976).

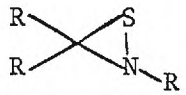
Description of Unpublished Research

1. Thione S-Imides.

We have continued our studies upon the various potential energy minima to be found on the surface for the valence isomerization, thione S-imide (1)⇌Thiazirane (2), as a function of substituent, R.



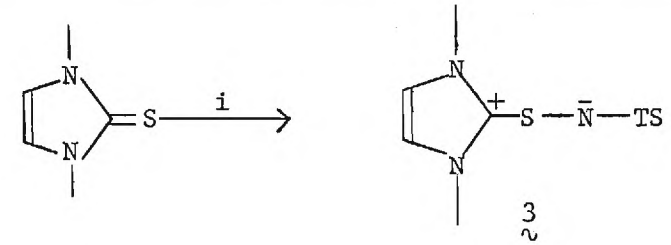
1



2

From molecular orbital calculations one may conclude that 1 represents a minima when a combination of electron donating and electron withdrawing substituents are present and otherwise 2 is the more stable isomer. This holds true for both the excited singlet and ground state.

Two examples of such stable "pull-push" substituted thione S-imides, 3 and 4, have been prepared by the method indicated.



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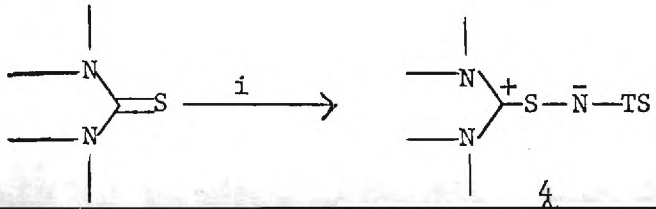
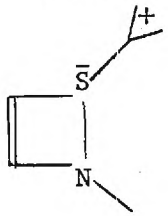
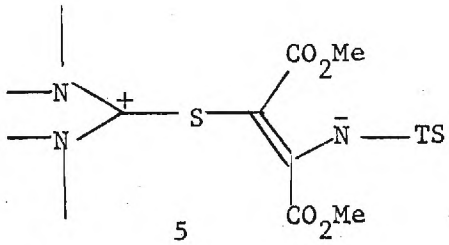


4

Both 3 and 4 when heated above 100° decompose to give the corresponding guaniclines and sulfur a reaction which is second-order in ylid and, therefore, does not proceed via a valence isomierzation - sulfur extrusion process. Photochemically, 3, undergoes this same reaction at -36°. A interesting cycloaddition reaction is observed when 4 is treated with dimethylacetylene dicarboxylate to give 5 whose structure was demonstrated by x-ray crystallography. This observed reaction requires



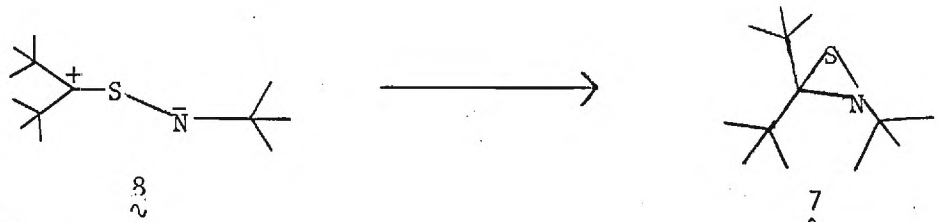
6



5

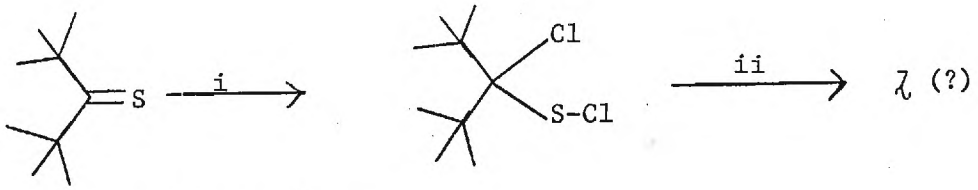
a rather novel heterocyclic intermediate, 6.

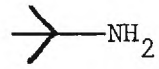
Turning to substituent unperturbed thione s-imides (or thiaziranes) we reasoned that the best opportunity to observe the more stable cyclic thiazirane isomer, 7, would be in the case of 8. Our synthesis proceeds



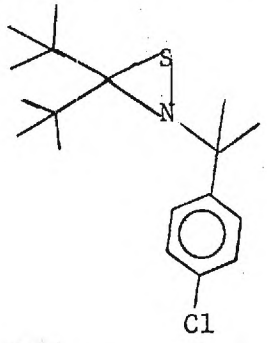
8 7

as follows:



i = Cl_2, -78°; ii = 

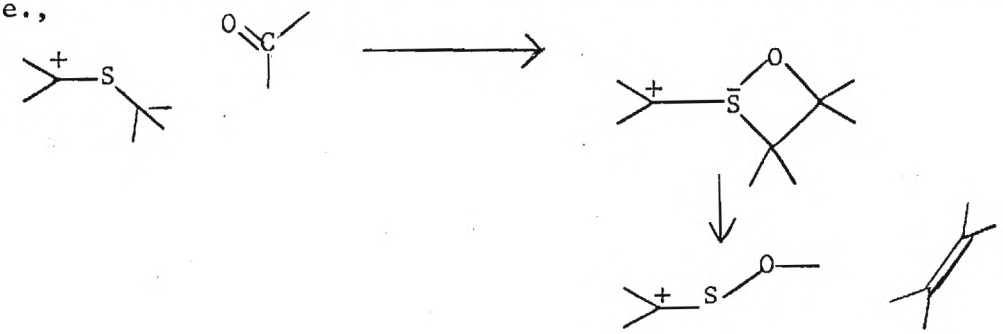
and we obtained an oil (mp ~5°) whose C^{13}-S shift was 100 ppm upfield of that observed for the known di-t-butylthione s-oxide which suggests structure 7. The low mp of this derivative precludes x-ray crystallography, at least at this facility, so 9 was prepared by an anlogous route and is a solid (mp ~45°) at room temperature. We are currently attempting to grow



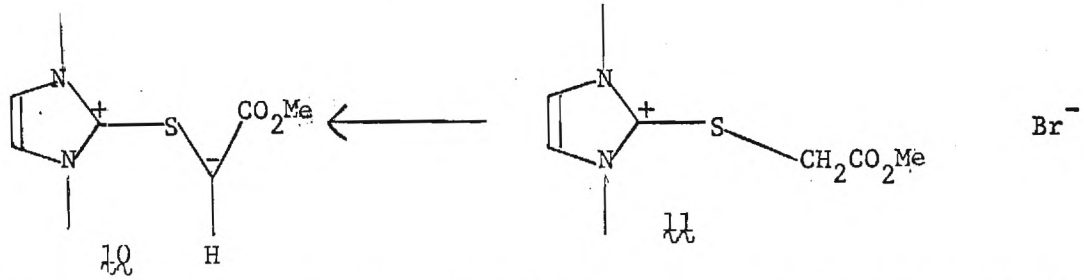
crystals suitable for a structure determination I intend to present this and subsequent work on S-N ylides at the symposium during the ACS meeting in Chicago (August 1977) before publication in a journal.

2. Thione S-Methylides

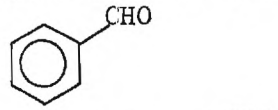
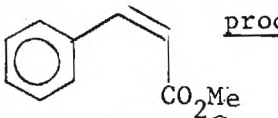
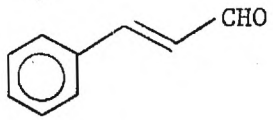
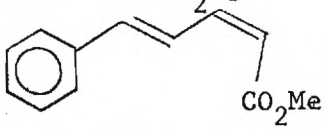
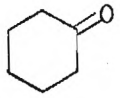
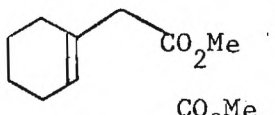
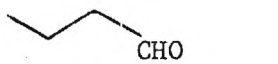
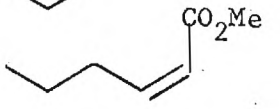
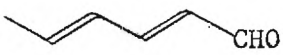
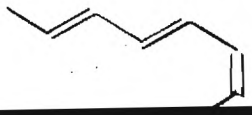
Aside from our published observations on this functional group we have explored the synthetic potential of reactions with carbonyl groups of aldehydes and ketones as a variant of the "Wittig Reaction", i.e.,



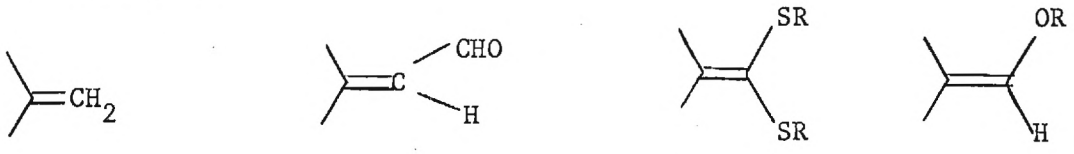
We have confined our studies so far, to the reagent, 10, generated in situ from the readily available salt, 11, and DBU as a base. Ylide 10 reacts



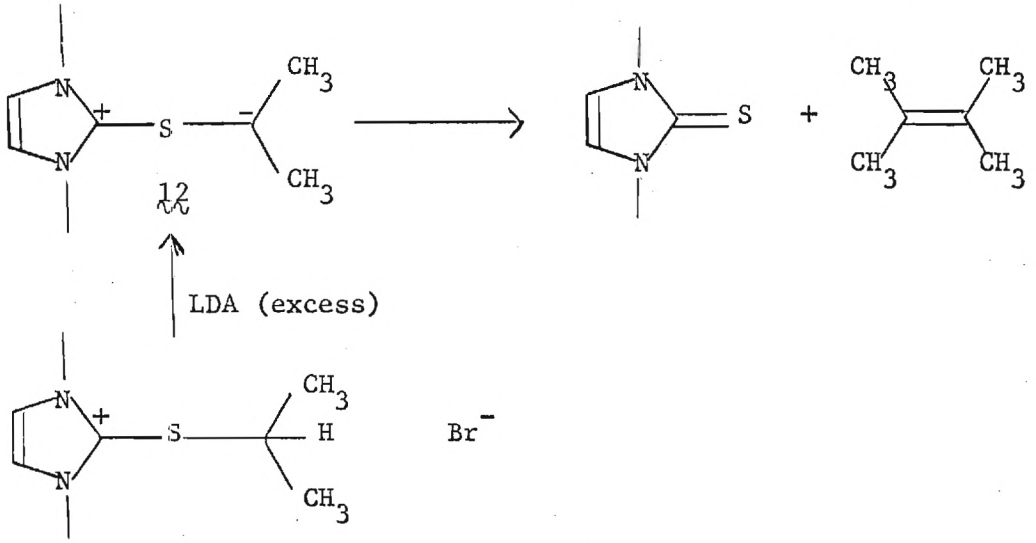
(-30° to 30°) readily with aldehydes to give α,β-unsaturated esters predominately with cis-stereochemistry, exactly opposite to what is observed in the Wittig reaction using carboalkoxyphosphoranes. This result suggests that our "quasi-Wittig" reaction will provide a unique synthetic method for the synthesis cis-acrylic esters. Some examples explored are:

reactant	product (yield)
	 (80)
	 (80)
	 (70)
	 (20)
	 (30)

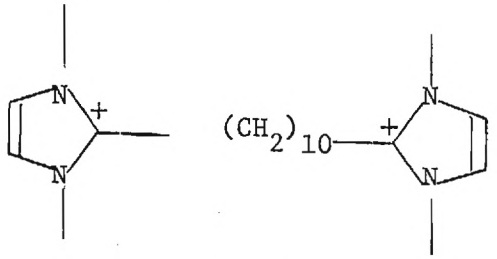
With such a promising start we will systematically investigate the full potential of this synthetic method for the conversion of ketones and aldehydes to such new functions as:



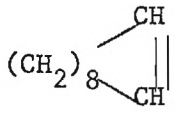
We noted some time ago that unstable thione S-methylides generated with good electron donating substituents but poor electron withdrawing substituents, such as 12, rapidly (even at -78°) underwent disproportionation to give alkenes and the precursor thione. The possibility exists that this reaction



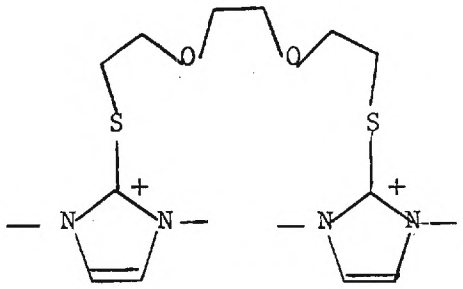
might provide a basis for a macrocyclic alkene synthesis and to this end we have prepared the bis-salts, 13 and 14, as possible precursors to 15 as the important funcitonalized crown ether 16 (here the Li^+ template effect on increasing the yield may be important).



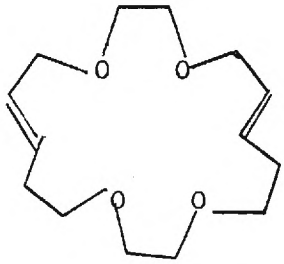
13



15



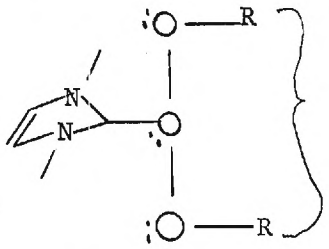
14



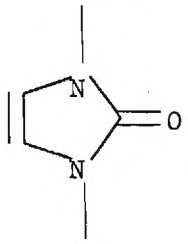
16

3. Hypervalent Molecules

The appendix contained a communication to the editor of the J. Amer. Chem. Soc. which is in press and reports the details of our studies on tricoordinate sulfuranes, a new class of hypervalent molecules. The theoretical analysis of the effect of substituents on stabilizing hypervalent bonding arrays suggests that one may be rewarded for a search among the first-row atoms for a stable example of a hypervalent species (a notion long held to be impossible by the uninitiated!). After consideration of all stabilizing "tricks" possible, molecule 17 (with R the most electron-withdrawing group available) has the best chance of chemical survival. However, we began our synthesis with 18 as a central intermediate and upon treatment with bromine obtained a

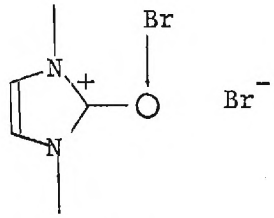


17

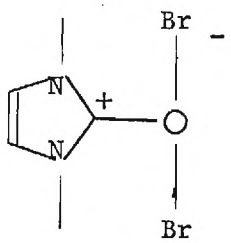


18

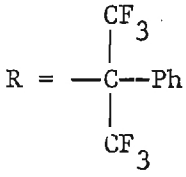
1:1 crystalline product, extremely sensitive to hydrolysis, which shows a typical imidazolium H^1 nmr and must be either 19 or 20. We have had



19



20

great difficulty growing crystals of a size suitable for x-ray analysis but will continue to try, and in the meantime, have the synthesis of 17 underway with R =  where the structure proof of hypervalency may also be

determined by nmr.